

REMARKS

Further and favorable reconsideration is respectfully requested in view of the foregoing amendments and the following remarks.

Claims 2, 4 and 6-9 were pending when examined. By this amendment, claims 2, 6, 8 and 9 are amended, and claims 4 and 7 are cancelled.

Claim 2 is amended to recite “A fullerene derivative fine wire composed of acicular crystal of a diethyl ester malonate derivative of C₆₀ and fullerene C₆₀, wherein the acicular crystal is monocrystalline”. Support for the amendments to claim 2 can be found on page 3, lines 10-14 and page 6, lines 5-6 of the specification.

Claim 6 is amended to recite “acicular crystal of a diethyl ester malonate derivative of C₆₀ and fullerene C₆₀”, and to correspond with the amendments to claim 2. Support for the amendments can be found on page 3, line 18 – page 4, line 3 of the specification.

Claims 8 and 9 are amended to depend only from claim 6, because claim 7 is cancelled.

I. Claim Rejections Under 35 U.S.C. § 103

A. Miyazawa '143, Beck et al. and Electron Microscopy

The Examiner rejects claims 2, 4 and 6-9 under 35 U.S.C. § 103(a) as being unpatentable over Miyazawa et al. (U.S. 2002/0192143) (“Miyazawa ‘143”) in view of Beck et al., and further in view of Miyazawa, Masuno and Suga (Electron Microscopy). As applied to the amended claims, Applicants respectfully traverse the rejection.

Miyazawa ‘143 discloses a method of making iodine-doped C₆₀ nano-whiskers by adding a solution of iodine/isopropyl alcohol to a solution of C₆₀ in toluene (see paragraphs [0262]-[0266]). The Examiner applies the Beck et al. reference for disclosing that fullerene C₆₀ forms a weak molecular complex with iodine (see Office Action, page 4, paragraph 2).

The Examiner acknowledges that Miyazawa ‘143 does not specifically teach the fullerene derivative recited claim 1 [Claim 1 had been cancelled, and Applicants presume the Examiner was referring to a diethyl ester malonate derivative of C₆₀, as recited in claim 2]. However, the Examiner asserts that the Electron Microscopy reference discloses a similar derivitizing process to make single crystal fullerene nano-whiskers of C₆₀ and malonic acid diethyl ester derivative, and that it would have been obvious to make single crystal fullerene nano-whiskers of C₆₀ of malonic acid diethyl ester derivative, because the resulting derivatives have smooth surfaces and

conduct high resolution (see Office Action, page 4, paragraphs 3-5). Applicants respectfully disagree.

Although Electron Microscopy discloses single crystal fullerene nano-whiskers of a C₆₀ malonic acid diethyl ester derivate, one of ordinary skill in the art would not have been motivated to combine the teachings of references. Regarding C₆₀ nano-whiskers, holes are formed along the growth axis of C₆₀ nano-whiskers (see Fig.6 of Jun-ichi Minato and Kun-ichi Miyazawa, "Solvated structure of C₆₀ nanowhiskers", Carbon, 43 [14] (2005) 2837-2841, copy enclosed). The holes have a diameter at the same level as those of C₆₀ molecules.

It is considered by those of ordinary skill in the art that iodine-doped C₆₀ nano-whiskers are formed by idonine entering the hole of the C₆₀ nano-whiskers. However, a diethyl ester malonate derivative of C₆₀ cannot fit into the hole of the C₆₀ nano-whiskers, because they are much bigger than the C₆₀ molecule.

Therefore, it would not have been predictable from the combination of Miyazawa '143, Beck et al. and Electron Microscopy to arrive at the fullerene derivative fine wire composed of acicular crystal of a diethyl ester malonate derivative of C₆₀ and fullerene C₆₀, wherein the acicular crystal is monocrystalline, and a manufacturing method of acicular crystal of a diethyl ester malonate derivative of C₆₀ and fullerene C₆₀, as recited in claims 2 and 6.

Accordingly, claims 2 and 6 would not have been obvious over the references.

Claims 8 and 9 depend from claim 6, and thus also would not have been obvious over the references.

B. Miyazawa '143, Beck et al. and Guldi et al.

The Examiner rejects claims 2, 4 and 6-9 under 35 U.S.C. § 103(a) as being unpatentable over Miyazawa '143 and Beck et al., and further in view of Guldi et al.

The Examiner states that "Miyazawa '143 does not specifically teach the fullerene derivative as per applicant claim 2" (see Office Action, page 6, paragraph 1).

However, the Examiner applies the Guldi et al. reference for teaching fullerene derivatives, such as "N-methodfulleropyrrolidine" (Applicants presume the Examiner intended "N-methyl-pyrrolidine") (see Office Action, page 6, paragraph 2).

Claim 2 is amended to delete "N-methyl-pyrrolidine", rendering the rejection of claim 2 moot.

Claim 6 is amended to “acicular crystal of a diethyl ester malonate derivative of C₆₀ and fullerene C₆₀”. As acknowledged by the Examiner, Miyazawa ‘143 does not specifically teach “a diethyl ester malonate derivative of C₆₀”. The Beck et al. and Guldi et al. references do not remedy this deficiency. Therefore, claim 6 would not have been obvious over Miyazawa ‘143 and Beck et al. and further in view of Guldi et al.

Claims 8 and 9 depend from claim 6, and thus also would not have been obvious over the references.

II. Conclusion

For these reasons, Applicants take the position that the presently claimed invention is clearly patentable over the applied references.

Therefore, in view of the foregoing amendments and remarks, it is submitted that the rejections set forth by the Examiner have been overcome, and that the application is in condition for allowance. Such allowance is solicited.

Respectfully submitted,

Kun'ichi MIYAZAWA et al.
/Andrew B.
By Frestein/

Respectfully signed by Andrew B.
Frestein
DN: cn=Andrew B. Frestein, o=WLP,
ou=WLP, email=afrestein@wenderoth.com
Date: 20091208133405-05'00

Andrew B. Frestein
Registration No. 52,917
Attorney for Applicants

ABF/rgf
Washington, D.C. 20005-1503
Telephone (202) 721-8200
Facsimile (202) 721-8250
December 8, 2009

Enclosure: Jun-ichi Minato and Kun-ichi Miyazawa, “Solvated structure of C₆₀ nanowhiskers”, Carbon, 43 [14] (2005) 2837-2841.

Solvated structure of C₆₀ nanowhiskers

Jun-ichi Minato ^{*}, Kun'ichi Miyazawa

Ecomaterials Center, National Institute for Materials Science, Namiki 1-1, Tsukuba 305-0044, Japan

Received 25 April 2005; accepted 7 June 2005

Available online 28 July 2005

Abstract

This work characterizes the structure of C₆₀ nanowhiskers prepared by the liquid–liquid interfacial precipitation method in the C₆₀-saturated *m*-xylene and isopropyl alcohol system. Transmission electron microscopy and X-ray diffraction measurement show that the C₆₀ nanowhiskers had a hexagonal structure with cell dimensions $a = 2.407$ nm and $c = 1.018$ nm which is different from pristine C₆₀. The structure of the C₆₀ nanowhiskers in solution is different from that of the solvated structure reported for the C₆₀ nanotubes but similar to that reported for the C₆₀ bulk crystal solvated with *m*-xylene. X-ray diffraction analysis also showed a shift to fcc structure after solvent evaporation. The C₆₀ nanowhiskers prepared using toluene as solvent also showed a similar solvated structure, and a more rapid structural change into fcc upon drying was again observed.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Carbon nanofibers; Fullerene; Infrared spectroscopy; Transmission electron microscopy; X-ray diffraction

1. Introduction

Crystalline fullerene solids precipitated from solutions sometimes show unexpected morphologies different from the ordinary face-centered cubic (fcc) packing of fullerene molecules [1,2], which may be attributed to the presence of solvent molecules between fullerene molecules. When isopropyl alcohol (IPA), which is known as a poor solvent of fullerenes, was gently added to a toluene solution saturated with C₆₀, needlelike or fibrous crystals were precipitated at the interface between the solutions [3]. Since their diameter was in the submicron range, they have been referred to as C₆₀ nanowhiskers and the preparation method have been referred to as liquid–liquid interfacial precipitation (LLIP) method. To date, the LLIP method has been successfully used to fabricate fullerene nanowhiskers from C₆₀ [3], C₇₀ [4,5] and C₆₀ derivatives [6,7]. The structure of the fullerene nanowhiskers have been understood based on the fcc

structure. The whisker axis (growth axis) is parallel to one of the closest-packed directions of C₆₀ molecules, i.e. (110) in the fcc structure. Since the intermolecular distance was observed to be shortened along this direction, a model was proposed where the '2 + 2' cycloaddition was assumed [3].

Most of the previous characterizations of the fullerene nanowhiskers were carried out on dried specimens [3–10]. However, fullerene molecules should be solvated when they are in true solution. It is known that many kinds of solvent form the structures of solid solvates with fullerenes [11–13] including toluene and *m*-xylene which are used in the LLIP method [9]. In addition, some of those solvated structures, depending on the kinds of solvent, have been shown to change into the fcc structure by the evaporation of solvent molecules in air [12,13]. It is thus expected that the fullerene nanowhiskers also have solvated structures when they are first precipitated from the liquid phase. However, few studies have examined the structure changes during drying of fullerene nanowhiskers from the LLIP method. In the present study, the C₆₀ nanowhiskers were prepared by the LLIP method using *m*-xylene and toluene as

^{*} Corresponding author. Tel./fax: +81 29 860 4669.
E-mail address: MINATO.Junichi@nims.go.jp (J.-i. Minato).

solvents. Characterizations by Fourier-transform infrared (FTIR) spectroscopy, transmission electron microscope (TEM) observation, and X-ray diffraction (XRD) measurement confirmed the solvated structure and the structural change in air for both of the specimens. The results were compared with the previous observations.

2. Experimental

The C_{60} nanowhiskers were prepared by the liquid-liquid interfacial precipitation method using *m*-xylene (or toluene) as solvent [9]. A typical procedure is as follows. Five milliliters of *m*-xylene (or toluene) solution saturated with C_{60} was put into a glass bottle and then 5 mL of IPA was gently added. The bottles were capped and kept at a temperature lower than 21 °C for more than one month before the characterization.

Morphological observations were performed using an ordinary optical microscope and a TEM (JEOL, JEM-2000EX). The specimens in the glass bottles were mounted on slide glasses or onto copper microgrids with carbon film using pipette. Infrared spectroscopy was performed for the C_{60} nanowhiskers and the pristine C_{60} powder with KBr using a FTIR apparatus (Valor III, JASCO, Tokyo, Japan). XRD spectra were obtained using an X-ray diffractometer (RIGAKU, RINT2000 Tokyo, Japan) with $CuK\alpha$ radiation.

3. Results and discussion

Fig. 1 shows an optical micrograph of the solid precipitates obtained by the liquid-liquid interfacial precipitation method in the C_{60} -saturated *m*-xylene and

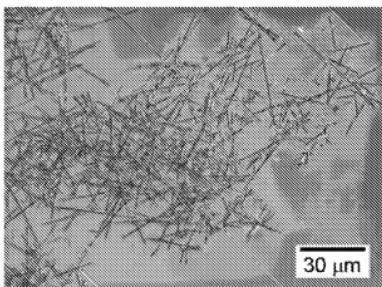


Fig. 1. Optical photomicrograph of C_{60} nanowhiskers prepared by the liquid-liquid interfacial precipitation method in the C_{60} -saturated *m*-xylene and isopropyl alcohol system.

IPA system. As shown in the image the precipitates were submicron in diameter and reached several tens of micrometers in length, i.e. nanowhiskers.

Fig. 2(a)–(c) shows FTIR spectra taken for the pristine C_{60} powder, the nanowhiskers grown in the C_{60} -saturated *m*-xylene and IPA system, and *m*-xylene, respectively. The spectra of Fig. 2(a) and (b) showed sharp absorption peaks characteristic of C_{60} (527, 576, 1182, and 1428 cm^{-1}), indicating that the specimens were composed of C_{60} molecules. However, the broad bands at 690 and 767 cm^{-1} indicated by circles in the spectrum of Fig. 2(b) suggest the presence of *m*-xylene molecules (Fig. 2(c)) trapped in the structure.

Fig. 3 shows a TEM image of a typical C_{60} nanowhisker grown in the C_{60} -saturated *m*-xylene and IPA system. Under TEM the C_{60} nanowhiskers were loosely curved by the contact with the carbon film support, indicating a similar flexibility as reported for the C_{60} nanowhiskers prepared using toluene as solvent [5]. However, the selected area electron diffraction patterns (SAEDPs) usually showed no coincidence with the fcc-based structure. Fig. 4(a) is an example of SAEDPs taken for the enclosed part of Fig. 3. The pattern resembles to that reported for the iodine-doped C_{60} whiskers [10] rather than to those for the C_{60} nanowhiskers [3] or the C_{60} nanotubes [14]. The SAEDPs taken with rotations around the growth axis consistently indicated that the lattice planes with a *d*-spacing close to 1 nm exist normal

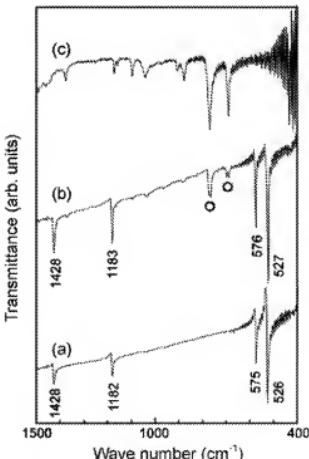


Fig. 2. FTIR spectra for (a) pristine C_{60} , (b) C_{60} nanowhiskers grown in the C_{60} -saturated *m*-xylene and isopropyl alcohol system, and (c) *m*-xylene.



Fig. 3. Transmission electron microscope image of a C_{60} nanowhisker grown in the C_{60} -saturated *m*-xylene and isopropyl alcohol system.

to the growth axis (Fig. 4(b)–(d)). By assuming a hexagonal symmetry, all the patterns were indexed with the direction [001] parallel to the growth axis. The ratio of the unit cell dimensions (a/c) was estimated to be 2.35. It is noted that the 0001 diffraction spots observed in the SAEDPs of Fig. 4(a), (c), and (d) disappeared when the specimen was rotated around [001] as shown in Fig. 4(b). This indicates that the 0001 spots were caused by the double diffraction, suggesting the 6_3 symmetry axis along [001].

To confirm whether the observed structure of the C_{60} nanowhiskers was solvated or not, the time dependence of XRD pattern was studied. For the measurement, the specimens were directly mounted on a glass sample holder immediately after the sampling from the glass bottles to observe the structural change during the drying process. The XRD pattern taken 29 min after the sampling from the glass bottles showed sharp peaks

(Fig. 5(a)). These peaks gradually became smaller and relatively broad peaks appeared (Fig. 5(b)). The former peaks were observed for up to 301 min; the latter peaks were at the similar positions as those for the pristine C_{60} (Fig. 5(e)) and indexed by a fcc system with the cell dimension $a = 1.423$ nm. This indicates that the structure was changed into fcc, from a solvated structure by the evaporation of solvent molecules in air. The pattern of Fig. 5(a) were different from that observed for the solvated structure of C_{60} nanotubes [14] and indexed by a hexagonal system with cell dimensions $a = 2.407$ nm and $c = 1.018$ nm ($a/c = 2.36$), which was consistent with the TEM observation.

A possible crystal structure suggested from the TEM and XRD results for the solvated structures of the C_{60} nanowhiskers is drawn in Fig. 6. In the figure, the fullerene molecules are represented as the spheres contacting with each other. Between the fullerene molecules lie the large channels along the c axis that can contain the solvent molecules. The packing structure may have symmetry as high as $P6_3/m$ if the positions of solvent molecules were not taken into account. This structure resembles to that reported by Ramm et al. [11] for the bulk crystals obtained through a slow evaporation of *m*-xylene and a mixture of carbondisulfide/*p*-*m*-xylene solutions of C_{60} (space group $P6_3$, $a = 2.3694(4)$ nm and $c =$

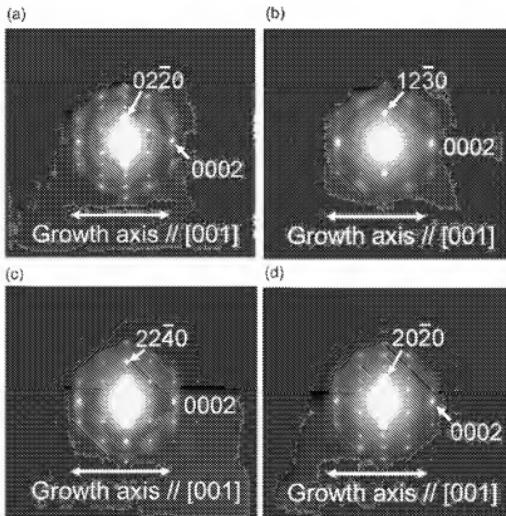


Fig. 4. Selected area electron diffraction pattern of the C_{60} nanowhisker taken for the enclosed part of Fig. 2 rotated by (a) 0° (b) 20.4° (c) 30.3° and (d) 55.7° around the growth axis, respectively; the incident beam directions are [100], [210], [110] and [010], respectively.

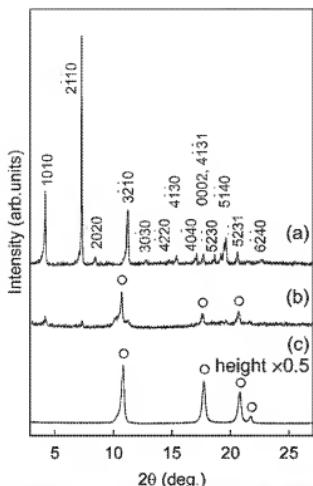


Fig. 5. X-ray diffraction patterns of C_{60} nanowhiskers grown in the C_{60} -saturated *m*-xylene and isopropyl alcohol system at (a) 29 min and (b) 301 min after sampling from the glass bottle. (c) X-ray diffraction pattern for pristine C_{60} . The peaks indicated by open circles correspond to the fcc structure of C_{60} .

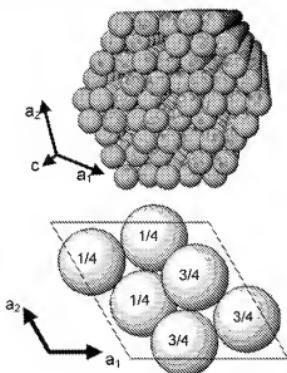


Fig. 6. Model for the hexagonal structure of solvated C_{60} nanowhiskers.

1.0046(2) nm at 100 K). Confirmation was thus made by the additional XRD measurement for the prismatic

crystals of C_{60} kept at 10 °C in the C_{60} -saturated *m*-xylene solution, resulting in the same patterns as observed for the present C_{60} nanowhiskers except for the stronger peak intensities of those reflections with $l \neq 0$ and broadening of each peak.

We also confirmed the similar structure and the structural change in air for the C_{60} nanowhiskers prepared using toluene as solvent, but the change was more rapid. The XRD pattern taken 29 min after the sampling from the glass bottles already had the peaks corresponding to the fcc structure (Fig. 7(a)). However, the other peaks than those for fcc were in the same positions as those observed for the C_{60} nanowhiskers prepared using *m*-xylene (Fig. 5(a)). These peaks were indexed by a hexagonal system with cell dimensions $a = 2.405$ nm and $c = 1.001$ nm. The structural change was completed within 69 min into fcc structure with a cell dimension $a = 1.420$ nm (Fig. 7(b)). The value was close to that for the pristine C_{60} ($a = 1.41$ nm, Fig. 7(c)). The different speed of the structural change between the C_{60} -nanowhiskers grown in the C_{60} -saturated *m*-xylene and IPA system and those grown in the C_{60} -saturated toluene and IPA system may be related to the vapor pressure difference between *m*-xylene and toluene.

It is remarkable that both structures before and after drying have a closest-packed direction of C_{60} molecules

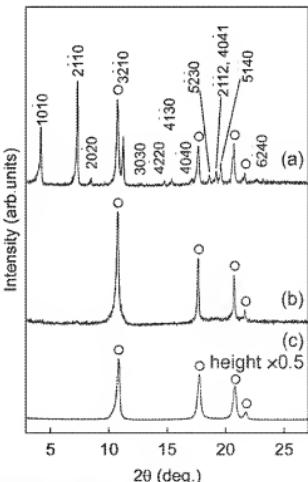


Fig. 7. X-ray diffraction patterns of C_{60} nanowhiskers grown in the C_{60} -saturated toluene and isopropyl alcohol system at (a) 29 min and (b) 69 min after sampling from the glass bottle. (c) X-ray diffraction pattern for pristine C_{60} . The peaks indicated by open circles correspond to the fcc structure of C_{60} .

parallel to the growth axes. This suggests that such a closest-packed chain act as a fixed structural unit during the transformation. When solvent molecules are extracted from the channels of the solvated structure, the chained structural units may shift perpendicularly to the growth axis to form a dense fcc structure keeping the periodicity along the growth axis.

It is likely that similar solvated structures may also have been present in previous studies [3–10]. The previous observations showed that the various fullerene nanowhiskers consistently had their growth axes parallel to one of the closest-packed directions of fullerene molecules with the intermolecular distances around 1.0 nm [3–10]. However, the deviation seems significant from specimen to specimen for the lattice plane spacings parallel to the growth axes such as (002) and (111) in the fcc system. For example, Miyazawa et al. pointed out that the lattice constants of $a = \sim 1.0$ nm and $c = \sim 2.0$ nm repeatedly appeared when a body-centered tetragonal structure was well fitted to a fast Fourier-transform pattern of a high-resolution TEM image for the C_{60} nanowhiskers [7]. In addition, Fujino et al. stated that more than two kinds of crystal structures were observed for the C_{60} nanowhiskers depending on the preparation conditions [8]. Some of these observations may in fact be consistent if a similar solvated structure as confirmed in the present study is assumed.

It seems that the solvated structure under TEM in vacuum were more stable than that observed by XRD in air though the specimens were from the same bottle. Probably, the interaction between C_{60} molecules was affected by the irradiation of electron beam [15] in the similar way as the photochemical polymerization observed during the Raman spectroscopic study [16]. If the structural change can be frustrated in this way, further applications such as adsorbents, catalysts, and membranes are expected for these microporous materials.

4. Summary

Structural characterizations were carried out for C_{60} nanowhiskers prepared by the liquid–liquid interfacial precipitation method in the C_{60} -saturated *m*-xylene and IPA system. TEM observation and XRD measurement showed that the C_{60} nanowhiskers had a hexagonal structure different from pristine C_{60} with cell dimensions $a = 2.407$ nm and $c = 1.018$ nm. The structure of the C_{60} nanowhiskers in solution was different from that of the solvated structure reported for the C_{60} nanotubes but similar to that reported for the C_{60} bulk crystal solvated with *m*-xylene. XRD measurement also showed the structural change into fcc in air accompanying the evaporation of solvent molecules. The C_{60}

nanowhiskers prepared using toluene as solvent also showed a similar solvated structure, but a more rapid structural change into fcc was observed.

Acknowledgement

The authors are grateful to Dr. Yutaka Takahashi (Mie University) for his helpful discussions.

References

- [1] Fleming RM, Kortan AR, Hessen B, Siegrist T, Thiel FA, Marsh P, et al. Pseudotetrahedral symmetry in pentane-solvated C_{60} and C_{70} . *Phys Rev B* 1991;44(2):888–91.
- [2] Yosida Y. Scanning electron microscope images of C_{60} whiskers. *Jpn J Appl Phys* 1992;31:L505–7.
- [3] Miyazawa K, Kuwasaki Y, Obayashi A, Kuwabara M. C_{60} nanowhiskers prepared by the liquid–liquid interfacial precipitation method. *J Mater Res* 2002;17(1):83–8.
- [4] Miyazawa K. C_{70} nanowhiskers by forming liquid/liquid interface in the systems of toluene solution of C_{70} and isopropyl alcohol. *J Am Ceram Soc* 2002;85(5):1297–9.
- [5] Miyazawa K, Hamamoto K, Nagata S, Suga T. Structural investigation of the C_{60}/C_{70} whiskers fabricated by forming liquid–liquid interface of toluene with dissolved C_{60}/C_{70} and isopropyl alcohol. *J Mater Res* 2003;18(5):1096–103.
- [6] Miyazawa K, Mashino T, Suga T. Structural characterization of the $C_{60}[\text{COOC}-\text{H}_2]$ whiskers prepared by the liquid–liquid interfacial precipitation method. *J Mater Res* 2003;18(11):2730–5.
- [7] Miyazawa K, Mashimo T, Suga T. Liquid phase synthesis of the nanowhiskers of fullerene derivatives. *Trans Mater Res Jpn* 2004;29(2):537–40.
- [8] Fujino M, Miyazawa K, Suga T. In situ observation of the behavior of C_{60} (nano)whiskers under heating by TEM. *Trans Mater Res Soc Jpn* 2004;29(5):1969–72.
- [9] Miyazawa K, Nishimura C, Fujino M, Suga T, Yoshii T. Fabrication and properties of fullerene nanowhiskers and nanofibers. *Trans Mater Res Soc Jpn* 2004;29(5):1965–8.
- [10] Miyazawa K, Hamamoto K. Formation of iodine-doped C_{60} whiskers by the use of liquid–liquid interfacial precipitation method. *J Mater Res* 2002;17(9):2205–8.
- [11] Raman M, Luger P, Zobel D, Duczek W, Boeyens JCA. Static disorder in hexagonal crystal structures of C_{60} at 100 K and 20 K. *Cryst Res Technol* 1996;31(1):43–53.
- [12] Collins C, Foulkes J, Bond AD, Klinowski J. Crystalline $C_{60} \cdot 2\text{CHBr}_3$ solvate: a solid-state study. *Phys Chem Chem Phys* 1999;1:5323–6.
- [13] Korobov MV, Stukalina EB, Mirakyan AL, Neretin IS, Slovokhov YL, Dzyabchenko AV, et al. New solid solvates of C_{60} and C_{70} fullerenes: the relationship between structures and lattice energies. *Carbon* 2003;41:2743–55.
- [14] Minato J, Miyazawa K, Suga T. Morphology of C_{60} nanotubes fabricated by the liquid–liquid interfacial precipitation method. *Sci Technol Adv Mater*, in press.
- [15] Zhao YB, Poirier DM, Pechman RJ, Weaver JH. Electron stimulated polymerization of solid C_{60} . *Appl Phys Lett* 1994;64(3):377–9.
- [16] Tachibana M, Kobayashi K, Uchida T, Kojima K, Tanimura M, Miyazawa K. Photo-assisted growth and polymerization of C_{60} nano-whiskers. *Chem Phys Lett* 2003;374:279–85.